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Magnetocapacitance without magnetoelectric coupling

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The existence of a magnetodielectric (magnetocapacitance) effect is often used as a test for multiferroic behavior in new material systems. However, strong magnetodielectric effects can also be achieved through a combination of magnetoresistance and the Maxwell-Wagner effect, unrelated to true magnetoelectric coupling. The fact that this resistive magnetocapacitance does not require multiferroic materials may be advantageous for practical applications. Conversely, however, it also implies that magnetocapacitance *per se* is not sufficient to establish that a material is multiferroic.

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There has been a recent surge of interest in the physics and applications of multiferroics.¹ Multiferroic materials are those where more than one ferroic order (magnetic, electric, or elastic) coexist and are coupled, but the term usually refers specifically to those with ferroelectric and magnetic order (magnetoelectrics). From the applied point of view, coupling between ferroelectricity and ferromagnetism would be useful for multistate memories, or memories with dual read-write mechanism, among other devices. From the fundamental point of view, the coexistence of ferroelectric and magnetic order also represents an interesting challenge, particularly since it has been shown that the conventional mechanism of ferroelectricity in perovskites, an off-centering of B-site cations (such as Ti⁴⁺ in BaTiO₃), requires the B site to have an empty *d* orbital, which is incompatible with magnetic ordering.²

In order to circumvent this incompatibility, two main routes are being investigated: (a) materials with nonconventional mechanisms for ferroelectric and/or magnetic ordering and (b) composite materials combining conventional ferroelectrics and ferromagnets segregated on a nanoscale level. Among the first are the so-called “geometric” magnetoelectrics such as hexagonal YMnO₃ (the true nature of ferroelectricity in this compound is still subject of controversy^{3–5}), highly frustrated spin systems such as TbMnO₃⁶ or TbMn₂O₅,⁷ and materials combining A-site (lone pair) ferroelectricity with B-site magnetic order, such as BiFeO₃⁸ and BiMnO₃.⁹ Examples of composites are the self-segregated clusters of magnetic CoFe₂O₄ and ferroelectric BaTiO₃,¹⁰ and superlattices combining ferromagnetic (La,Ca)MnO₃ with ferroelectric BaTiO₃.¹¹

Establishing magnetoelectric coupling requires measuring the effect of a magnetic field on ferroelectric polarization or, conversely, that of an electric field on magnetic order. A difficulty in achieving this lies in that many candidates to be magnetoelectric are in fact poor insulators, which makes it difficult for them to sustain the electric fields necessary to switch polarization.^{12,13} A relatively simple and thus widely used alternative characterization method consists in measuring the dielectric constant (ϵ) as a function of temperature (*T*) and/or magnetic field (*B*). In a magnetoelectric, magnetic order is coupled to polarization and thus to the dielectric

constant as well. Measuring $\epsilon(T)$ and looking for deviations around the magnetic transition can therefore be used to detect a multiferroic state.^{14,15} Since magnetic field affects magnetic ordering, the field also indirectly alters the dielectric constant of magnetoelectric multiferroics. This is the so-called magnetodielectric (or magnetocapacitance) effect, which has been reported for a wide range of materials.^{11,15–20} The problem with this approach, however, is that magnetoelectric coupling is not the only way to produce magnetocapacitance: as shown in this letter, magnetoresistive artifacts can also give rise to an apparently large magnetodielectric effect. Thus, while multiferroicity may imply magnetocapacitance, the converse is not true.

For the (acoustic frequency) dielectric constant to be measured in a multiferroic system, a capacitor structure has to be made so that an ac electric field can be applied to it. The response to the electric field will contain at least one capacitive (dielectric) term and one resistive (leakage) term. Since the work functions of electrode and dielectric material are rarely identical, band bending may occur near the electrode-dielectric interfaces, causing charge injection from the electrode into the dielectric or vice versa (charge depletion). In either case, the result is a layer near the electrode interface with a different density of charge carriers, and hence different resistivity than that of the core. If the dielectric is not a very good insulator, this can cause the electric field to be mostly dropped in the charge-depleted interfacial area rather than in the core of the material, yielding artificially high apparent dielectric constants. This effect has been documented in several oxide materials, including manganites,^{20–22} and may happen not only at dielectric-electrode interfaces but also at grain boundaries in ceramics²³ and interslab interfaces in superlattices.²⁴

Whether the heterogeneous nature of the sample is accidental (interfacial or grain-boundary layers), or deliberate (superlattices), either case can be described by the Maxwell-Wagner (M-W) capacitor model. This effectively consists of two leaky capacitors in series (Fig. 1). The impedance of such a system under an ac field is a complex quantity, and the real and imaginary parts of its permittivity are^{24,25}

$$\epsilon'(\omega) = \frac{1}{C_0(R_i + R_b)} \frac{\tau_i + \tau_b - \tau + \omega^2 \tau_i \tau_b \tau}{1 + \omega^2 \tau^2}$$

and

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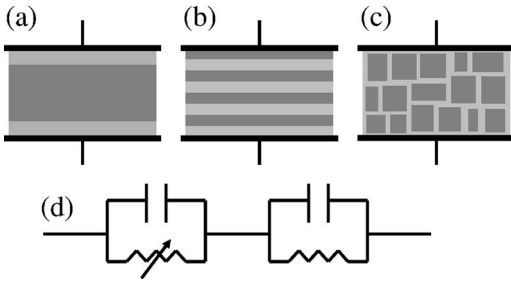


FIG. 1. Capacitor systems with magnetoresistive Maxwell-Wagner behavior: (a) homogeneous material with charge-depleted interfacial layers, (b) superlattice, and (c) clustered material or fine-grained ceramic with depleted grain boundaries. All can be modeled by two leaky capacitors in series with one of the leakage components being magnetically tunable (d).

$$\varepsilon''(\omega) = \frac{1}{\omega C_0(R_i + R_b)} \frac{1 - \omega^2 \tau_i \tau_b + \omega^2 \tau(\tau_i + \tau_b)}{1 + \omega^2 \tau^2},$$

where subindexes i and b refer to the interfacial-like and bulk-like layers, respectively, R =resistance, C =capacitance, $\omega=2\pi$ frequency, $\tau_i = C_i R_i$, $\tau_b = C_b R_b$, $\tau = (\tau_i R_b + \tau_b R_i)/(R_i + R_b)$, $C_0 = \varepsilon_0 A/t$, A =area of the capacitor, and t =thickness. In these equations the absolute thickness is actually irrelevant, what counts instead is the thickness ratio t_i/t_b .^{24,25}

If the resistance of any of the layers is changed by a magnetic field, so will the measured permittivity. Magnetoresistance (MR) combined with the Maxwell-Wagner effect thus provides a mechanism for magnetocapacitance in materials that are not necessarily multiferroic.

By way of example, let us examine the case of a manganite-based MR material, with charge-depleted (high resistivity) interfacial regions. The MR of manganites is known to have different contributions from the boundaries and from the core of the sample.^{26,27} Here, the two limiting cases have been considered: a ceramic where MR is dominated by spin-polarized tunneling across grain boundaries,^{26,27} and a thin film or single crystal where the MR is due to double exchange in the core of the sample.^{28,29} It is worth mentioning that the present model requires only that within a material system there exist regions with different MR responses, which happens not only in boundary layers, but also when there are phase-separated clusters, as in some mixed-valence manganites,²⁰ and possibly also in relaxor-like selenides.¹⁶

In the present calculations we have assumed a core resistivity of $\sim 10^5 \Omega \text{ m}$ (typical of undoped compounds such as BiMnO_3 ¹³ and YMnO_3 ¹⁵), with boundary layers having a resistivity 100 times higher and $t_i/t_b=0.1$. The intrinsic (dipolar) dielectric constant is in principle the same for interface and bulk, $\varepsilon_r \sim 25$ being a representative figure.^{6,7,14-17} Negative magnetoresistance is well described by $R(B)/R(0) \sim \exp(-B/B_S)$,^{27,28} ($B_S=2 \text{ T}$ has been used). While mixed-valence manganites can display colossal MR, the MR of undoped materials such as TbMnO_3 , BiMnO_3 , and YMnO_3 has not, to this author's knowledge, been reported, and may well be smaller than assumed here, if at all present; accordingly, the MR contribution to their magnetocapacitance could be small, or absent. It is nonetheless worth mentioning that the mixed-valence required for double-exchange MR can be induced not only by doping, but also by oxygen vacancies in undoped compounds.

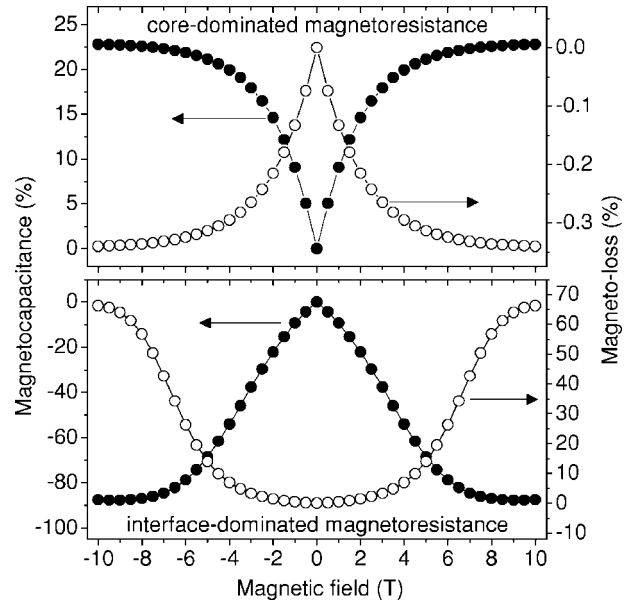


FIG. 2. Calculated magnetocapacitance (full circles) and magnetolosses (empty circles) of a magnetoresistive material with depleted boundary layers when the MR is core-based (e.g., double-exchange mechanism) and interface-based (e.g., tunneling magnetoresistance).

With the help of the M-W equations it is now possible to calculate the magnetocapacitance, defined as

$$\text{MC} = \frac{\varepsilon'(B) - \varepsilon'(0)}{\varepsilon'(0)} \times 100,$$

and the magnetolosses, defined as

$$\text{ML} = \frac{\tan \delta(B) - \tan \delta(0)}{\tan \delta(0)} \times 100,$$

where $\tan \delta = \varepsilon''/\varepsilon'$. The results for $\omega=1 \text{ kHz}$ are shown in Fig. 2.

Three features are noteworthy. First, giant MR can yield giant magnetocapacitance. Second, the sign of the magnetocapacitance depends on whether the (negative) MR takes place at the interfaces or at the core. Finally, the magnetoresistance directly affects the dielectric loss. Careful examination of magnetolosses, unfortunately absent from much of the literature, can therefore be useful in clarifying resistive effects.

Another useful example is that of a superlattice combining a purely ferroelectric material with a purely magnetoresistive one. Here, the relative dielectric constants of the two components are different, typically $\varepsilon_r \sim 250$ for barium titanate films and $\varepsilon_r \sim 25$ for manganites. The resistivity of ferroelectric thin films is usually in the range 10^4 – $10^8 \Omega \text{ m}$ ($10^6 \Omega \text{ m}$ has been assumed). In Fig. 3, $\varepsilon'(\omega)$ and $\tan \delta(\omega)$ are plotted with and without applied magnetic field for a superlattice with $t_i/t_b=1$. Qualitatively, the frequency dependence is very similar to that reported for superlattices,¹¹ although the sign of the magnetocapacitance is different. MR has been assumed here to reside in the manganite layers, but spin-dependent tunneling across the ferroelectric is also possible, as is magnetic tuning of size of the depletion layers at the manganite-titanate junctions;³⁰ in either case the sign of the magnetocapacitance would be the opposite of that calculated here.

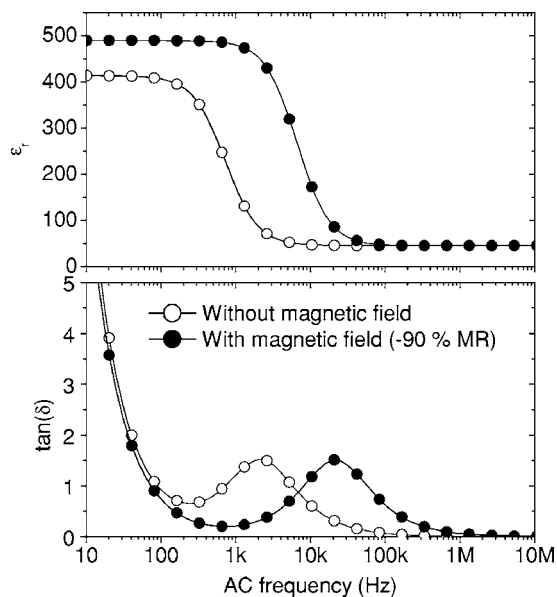


FIG. 3. Calculated relative dielectric constant and dielectric loss as a function of frequency for a superlattice consisting of ferroelectric barium titanate and a magnetoresistive manganite.

The frequency dependence can be interpreted as follows. At high frequencies charge carriers do not have time to respond to the field, so that the measured capacitance is simply that of two (insulating) capacitors in series. At low frequencies, on the other hand, the charge carriers in the low resistivity layer do respond, so that most of the field is dropped across the layers with bigger resistivity, and thus the apparent decrease in dielectric thickness results in an increased capacitance. This provides another rule of thumb: unless very slow dynamics (such as in glasses) are involved, intrinsic magnetocapacitance should be measurable at frequencies faster than the conductivity cutoff (RC time constant). It is also worth noticing that the magnetocapacitance is maximal around the $1/RC$ frequency. Since resistance changes with temperature, $MC(T)$ will show a peak when $1/RC$ coincides with the measurement frequency. The temperature-frequency behavior can also mimic that of relaxors, when in fact it is a resistive artifact.²⁴

In sum, the calculations show that large (colossal) magnetodielectric effects can be achieved in material systems without true magnetoelectric coupling. This has the practical advantage that the otherwise rare multiferroic materials are not needed to achieve it, although high losses would normally be concomitant. Conversely, measuring a magnetodielectric effect is in principle insufficient to establish conclusively the existence of magnetoelectric coupling, unless accompanied by careful examination of dielectric losses and frequency dependence. Needless to say, the fact that magnetoresistance can give rise to magnetocapacitance by no means implies that magnetocapacitance always has a resistive origin. However, it does imply that evidence

based solely on dielectric measurements should be handled with care.

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